STUDY IN THE DIARYL ACYL HYDRAZINE SERIES: SALT FORMATION IN THE BENZIDINE AND SEMIDINE REARRANGEMENTS

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Doctor of Philosophy

BY

FRANK OLIN RITTER, A. B., M. A.

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ACKNOWLEDGMENT

This investigation was carried out under the direction of Professor John J. Ritter, to whom the author is greatly indebted for his generous assistance and helpful criticism throughout the course of the research.

DEDICATED TO

MY WIFE AND DAUGHTER

[Reprint from the Journal of the American Chemical Society, 52, 2815 (1930).]

[Contribution from the Chemical Laboratory of the Washington Square College of New York University]

STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. I

By John J. Ritter and Frank O. Ritter

Received November 5, 1929 Published July 3, 1930

The diaryl acyl hydrazines of the type $ArNCOCH_3NHAr$ have been hitherto little investigated. The only previously known members of this series are mono-acetylhydrazobenzene,[1] mono-acetylbenzene-hydrazo-*p*-toluene,[2] and mono-acetylhydrazo-*p*-toluene.[1]

The acetylation of aromatic hydrazo compounds, by means of which the members of this group may be prepared, was undertaken by us to gain some knowledge of the relative reactivities of the N atoms of the hydrazo linking in unsymmetrical members of the series, of the type Ar'NHNHAr. The behavior of hydrazo compounds on rearrangement in acid solution has been thoroughly investigated[3] with reference to the effect of the presence of the more common substituent groups in the aryl nuclei. The effect of such structural modifications upon the hydrazine residue, however, has not previously been studied; it has been found possible by us to detect such changes by treatment with acetic anhydride, which had previously been shown, in the cases cited above, to yield mono-acetyl derivatives readily. We have therefore prepared and studied several of the mono-acetyl derivatives of the unsymmetrical hydrazobenzenes from this point of view.

The structures of these compounds were determined by reduction with phenylhydrazine. The present paper describes the preparation and identification of these compounds; an alternative method of identification involving oxidation of the acetyl derivatives, with the description of some new members of this series, and the bearing of this research upon the rearrangement of hydrazo compounds in acid solution, will be presented in a later communication. Of the compounds described here it was found that each of the following yields two isomeric mono-acetyl derivatives in approximately equal amounts: benzene-hydrazo-*p*-toluene, *p*-chlorohydrazobenzene and *p*-bromohydrazobenzene. Benzene-hydrazo-*o*-toluene yields a single mono-acetyl derivative. It is of interest to note also that we have observed in this series the kind of isomerism shown by monobenzoylhydrazobenzene, and described by Freundler.[4] Mono-acetyl-*p*-bromohydrazobenzene was isolated in three forms, one of which changed gradually into one of the others during several weeks.

The reduction of the mono-acetylhydrazo compounds by phenylhydrazine severs the nitrogen atoms of the hydrazo linking, yielding the corre-

[1] Stern, *Ber.*, **17**, 380 (1884); Goldschmidt and Euler, *ibid.*, **55**, 616 (1922).

[2] Jacobson and Lischke, *Ann.*, **303**, 370 (1898).

[3] Jacobson, *ibid.*, **428**, 90–99 (1922).

[4] Freundler, *Compt. rend.*, **136**, 1554 (1903).

sponding amine and anilide. The reduction products are easily separated by treatment with dilute acetic acid, in which the amine dissolves while the amide remains undissolved. This reduction method has been applied successfully to the mono-acetyl derivatives of hydrazobenzene and benzene-hydrazo-*o*-toluene, and to one of each of the two isomeric mono-acetyl derivatives of benzene-hydrazo-*p*-toluene, *p*-chlorohydrazobenzene and *p*-bromohydrazobenzene.

In our early experiments attempts were made to follow the reduction and judge of its completeness by measuring the volume of nitrogen evolved during the reaction, since phenylhydrazine on oxidation yields nitrogen as shown by the equation

$$C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + 2H$$

The volume of nitrogen evolved was in most cases less than the theoretical. Further addition of phenylhydrazine to the partly reduced acetylhydrazo compound resulted in the evolution of more nitrogen, even after an amount far in excess of the theoretical one mole had been added. Ammonia was also detected among the gaseous products of the reaction. These facts made it evident that the phenylhydrazine, in addition to its reaction with the acetylhydrazo compound, was undergoing self-oxidation–reduction

$$2C_6H_5NHNH_2 \longrightarrow C_6H_6 + N_2 + NH_3 + C_6H_5NH_2$$

Considering that phenylhydrazine boils at 242° with only slight decomposition, it seemed remarkable that decomposition should take place so readily at the temperature of these experiments (160–180°). In one experiment the rate of evolution of the nitrogen was measured and was found to increase rapidly for a time, as the reduction of the acetyl hydrazo compound progressed. It was evident that one of the reaction products catalyzed the self-oxidation–reduction of phenylhydrazine. A study of the behavior of phenylhydrazine at 160° in the presence of acetanilide and at 185° in the presence of acet-*m*-toluidide showed that both of these substances bring about rapid decomposition of the phenylhydrazine, while undergoing no change themselves. A similar effect has been reported by Just,[5] who observed that sulfanilic acid accelerated the self-oxidation–reduction of phenylhydrazine. A procedure, to be described in the experimental part, was finally developed whereby complete reduction of the hydrazo compound may be recognized.

For convenience in describing the acetylhydrazo compounds in the experimental part, the nitrogen atoms of the hydrazo linking will be designated as N and N′, N referring to the nitrogen atom attached directly to the unsubstituted benzene nucleus.

Experimental Part

The unsymmetrical hydrazo compounds were prepared by reduction of the corre-

[5] Just, *Ber.*, **19**, 1207 (1886).

sponding azo compounds, the latter having been obtained by Wieland's[6] modification of Baeyer's[7] method. Treatment of the hydrazo compounds with acetic anhydride resulted in the mono-acetyl derivatives. The general procedures, which were substantially the same in all cases, will be briefly outlined.

Preparation of the Azo Compounds.—Equimolar amounts of nitrosobenzene and the appropriate amine were condensed according to Wieland's procedure. In practically all cases nearly pure crystalline products were readily obtained in yields of about 80% of the theoretical: **benzene-azo-*p*-toluene,** m. p. 71–72°, in agreement with Mills;[8] **benzene-azo-*o*-toluene,** b. p. 156–158° (corr.) at 4 mm. (Jacobson[9] reported this substance as a liquid at ordinary temperature); ***p*-chloro-azobenzene,** m. p. 88°, in agreement with Heumann and Mentha;[10] ***p*-bromo-azobenzene,** m. p. 88°, in agreement with Jacobson and Grosse.[11]

Preparation of the Hydrazo Compounds.—The azo compounds were reduced with zinc dust and glacial acetic acid in boiling alcohol. This method was found to be more convenient than that of Jacobson and Lischke[2] in which reduction was accomplished with zinc dust and sodium hydroxide solution. The procedure in a typical experiment was as follows. Glacial acetic acid was added dropwise to a mixture of zinc dust and a 10–15% solution of the azo compound in boiling 95% alcohol until the solution became colorless. The solution was filtered hot and the filtrate cooled rapidly in an ice-bath. In some cases the hydrazo compound crystallized from the cold solution; in others, it was necessary to add ice water slowly to the alcoholic solution to bring about precipitation. The crystals were filtered and allowed to dry. The solvent evaporates rapidly from the crystalline products obtained in this way and the danger of air oxidation to the azo compound is thus greatly minimized. The products obtained by this procedure were colorless and apparently quite free from the azo compounds: **benzene-hydrazo-*p*-toluene,** m. p. 87–88° (Jacobson and Lischke[2] give 86–87°); **benzene-hydrazo-*o*-toluene** m. p. 101–102°, in agreement with Jacobson;[9] ***p*-chlorohydrazobenzene,** m. p. 90–91° (Heumann and Mentha[10] report 89–90°); ***p*-bromohydrazobenzene,** m. p. 115° in agreement with Janowsky and Erb.[12]

Acetylation of the Hydrazo Compounds.—The procedure described by Stern[13] was employed. One part of the hydrazo compounds was dissolved in about three parts of freshly distilled acetic anhydride, and the mixture allowed to stand for several hours, usually overnight. The resulting solution was then added to about five parts of water and well shaken. The acetyl derivatives separated either as crystalline solids or as viscous oils which slowly solidified on standing. It was found that the structurally isomeric acetyl derivatives, when formed, could be separated by recrystallization from 95% alcohol. One of the isomers in each case was found to crystallize from the hot solution on cooling, while the second could be isolated by slow spontaneous evaporation of the mother liquor. As a class these compounds are colorless crystalline solids, rather soluble in alcohol, ether, chloroform and boiling benzene, and sparingly soluble in water and in ligroin.

N'-Acetylbenzene-hydrazo-*p*-toluene, m. p. 140–141° (corr.) in agreement with Jacobson and Lischke.[2]

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[6] Wieland, *Ber.*, **48,** 1107 (1915).
[7] Baeyer, *ibid.*, **7,** 1639 (1874).
[8] Mills, *J. Chem. Soc.*, **67,** 930 (1895).
[9] Jacobson, *Ber.*, **28,** 2544 (1895).
[10] Heumann and Mentha, *ibid.*, **19,** 1687 (1886).
[11] Jacobson and Grosse, *Ann.*, **303,** 320 (1898).
[12] Janowsky and Erb, *Ber.*, **20,** 358 (1887).
[13] Stern, *ibid.*, **17,** 380 (1884).

N-Acetylbenzene-hydrazo-*p*-toluene, needles, m. p. 124°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.75.

N-Acetylbenzene-hydrazo-*o*-toluene, m. p. 78°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: N, 11.66. Found (micro-Dumas): N, 11.47.

N-Acetyl-*p*-chlorohydrazobenzene, m. p. 123–124°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.62.

N′-Acetyl-*p*-chlorohydrazobenzene, m. p. 111–112°.

Anal. Calcd. for $C_{14}H_{13}ON_2Cl$: N, 10.74. Found (micro-Dumas): N, 10.82.

N′-Acetyl-*p*-bromohydrazobenzene, m. p. 83°, prisms from 90–120° ligroin.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 8.97.

N-Acetyl-*p*-bromohydrazobenzene, rosets of prismatic crystals from alcohol, m. p. 117–118°.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.42.

Isomeric Form of N-Acetyl-*p*-bromohydrazobenzene.—In the course of one experiment, N-acetyl-*p*-bromohydrazobenzene was recrystallized from alcohol containing about 10% of benzene. In addition to the N-acetyl derivative already described, a second product consisting of large cubical crystals was deposited on spontaneous evaporation of a part of the mother liquor. This substance melted at 88–89°. It was analyzed directly after isolation.

Anal. Calcd. for $C_{14}H_{13}ON_2Br$: N, 9.18. Found (micro-Dumas): N, 9.70.

After standing for two or three months in a closed vessel, the cubical crystals were found to have crumbled slowly to a white opaque powder. The latter melted at 117–118° and was identical with the stable N-isomer.

Identification of the Acetyl Derivatives.—A small amount (3–5 g.) of the acetyl derivative was heated with an equimolar amount of phenylhydrazine at 180° until the evolution of nitrogen and ammonia had ceased. This usually required about six hours. The mixture was then dissolved in 2–3 cc. of glacial acetic acid with slight warming and then treated with 5 cc. of water. The amide was precipitated as an oil which slowly solidified. The solid mass was then recrystallized from benzene or toluene. In those cases where isomeric compounds were obtained, one of the isomers only was identified by this procedure. The identity of the second isomer was established from the following considerations: (1) its non-identity with the first, (2) analysis, (3) transformation to the azo compound by hydrolysis of the acetyl group followed by oxidation with hydrogen peroxide. The following members of the above series were identified by phenylhydrazine reduction: N′-acetylbenzene-hydrazo-*p*-toluene, N-acetylbenzene-hydrazo-*o*-toluene, N′-acetyl-*p*-chlorohydrazobenzene and N′-acetyl-*p*-bromohydrazobenzene.

Effect of Anilides on the Self-oxidation–Reduction of Phenylhydrazine.—The reduction of N-acetylbenzene-hydrazo-*o*-toluene was conducted in one experiment to secure an approximate measure of the rate of evolution of nitrogen; 0.566 g. of the substance and 0.25 g. of phenylhydrazine were heated at 175–180° and the nitrogen evolved was collected over dilute hydrochloric acid in an inverted graduated cylinder. The volumes (cc.) evolved during successive five-minute intervals were (uncorr.): 5.0, 9.5, 12.5, 10.0, 7.0, 6.0, 4.0. The rapid increase in rate during the first fifteen minutes suggested the following experiments on the effect of acetanilide and acet-*m*-toluidide in the self-oxidation–reduction of phenylhydrazine.

(a) **Acetanilide.**—1.35 g. of acetanilide and 1.08 g. of phenylhydrazine were heated at 185° and the evolved gases collected over water in a graduated cylinder. The presence of ammonia in the gaseous products was detected by its odor and action on litmus,

and a layer of benzene appeared on the surface of the water in the graduated cylinder. After the reaction had ceased, 110 cc. of nitrogen (corrected for temperature, pressure, water vapor and benzene vapor) had been collected. This corresponds almost exactly to the volume of nitrogen theoretically obtainable by the self-oxidation–reduction of phenylhydrazine (112 cc.). The reaction mixture solidified on cooling. The crystals after washing with benzene melted at 114–115° and were shown to be acetanilide by comparison with an authentic sample of the latter.

(b) **Acet-*m*-toluidide.**—0.822 gram of acet-*m*-toluidide and 0.608 g. of phenylhydrazine were heated at 150–160°, as in (a). The nitrogen evolved measured 63 cc. (corr.); the theoretical nitrogen volume is 63 cc. The reaction mixture was dissolved in 1 cc. of glacial acetic acid and the solution slowly diluted with 5 cc. of water. An oil separated which was washed with hot water and allowed to cool. It was then seeded with a small crystal of acet-*m*-toluidide and allowed to stand for twenty-four hours. The oil solidified completely; the crystals were pressed dry on filter papers and found to melt at 67–68°. The crystalline product was acet-*m*-toluidide which underwent no change during the reaction.

Modified Procedure for Reduction with Phenylhydrazine.—The point at which the reduction of the acetylhydrazo compound with phenylhydrazine is complete was determined in the case of a mono-acetylbenzene-hydrazo-*m*-toluene (not described in this communication) in the following manner: 1.33 g. (1 mol) of acetylhydrazo compound and 1.8 g. (3 mols) of phenylhydrazine were heated at 160° until gases ceased to be evolved. Then 0.16 g. of phenylhydrazine was added, the mixture again heated and the evolved nitrogen collected and measured. It was found that 25 cc. (corr.) was evolved; 0.16 g. of phenylhydrazine should yield 16.6 cc. when undergoing complete self-oxidation–reduction; the reduction of the acetyl hydrazo compound was therefore incomplete. An additional 0.16 g. of phenylhydrazine was added, the heating continued at 160°, and the volume of nitrogen again measured. This time 17.1 cc. (corr.) was collected, indicating that the reduction was practically complete, inasmuch as the newly added phenylhydrazine underwent only self-oxidation–reduction.

Summary

1. Several new diaryl acyl hydrazines have been prepared.
2. A method for their identification has been described.
3. The self-oxidation–reduction of phenylhydrazine has been shown to be accelerated by acetanilide and acet-*m*-toluidide.

New York, N. Y.

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[Contribution from the Chemical Laboratory of the Washington Square College of New York University]

STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. II. SALT FORMATION IN THE BENZIDINE AND SEMIDINE REARRANGEMENTS

By John J. Ritter and Frank O. Ritter

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In a previous paper[1] the authors described several unsymmetrical diaryl acetyl hydrazines, with a method for determining their structures based upon reduction with phenylhydrazine. The present communication treats of additional new members of this series, the determination of their structures by oxidation with potassium dichromate in glacial acetic acid solution, and the bearing of this work upon the problem of salt formation in the benzidine and semidine rearrangements.

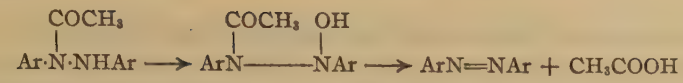
The oxidation of diaryl acetyl hydrazines has been investigated by Goldschmidt and Euler,[2] who reported the formation of tetrazanes by the oxidation of mono-acetylhydrazobenzene and mono-acetylhydrazo-*p*-toluene in benzene solution with lead dioxide. We have carried out the oxidation of the latter hydrazo compounds and also those described in our previous paper[1] with potassium dichromate in glacial acetic acid at ordinary temperature, and have found that tetrazanes are not formed under these conditions in any case. Two kinds of behavior on oxidation were shown by the acetylhydrazo compounds examined by us. All of the mono-acetylhydrazines previously identified by phenylhydrazine reduction[1] were oxidized with dichromate and were found to divide themselves with reference to behavior on oxidation into two series. The N-acetyl[3] derivatives were oxidized in all cases to the corresponding azo compounds, while the N′-derivatives gave brilliant, intensely colored red or violet solutions from which highly colored crystalline products were isolated.

The production of the colored oxidation products appears to depend upon the presence of the group , since the oxidation of mono-acetyl-hydrazo-*p*-toluene was found to yield, like the N-acetyl derivatives of the unsymmetrical members studied, the corresponding azo compound. The colored oxidation product derived from mono-acetylhydrazobenzene is under investigation in this Laboratory, and its structure has been established with some certainty. The oxidation of the N-derivatives probably takes place through the steps

[1] John J. Ritter and Frank O. Ritter, This Journal, 52, 2815 (1930).

[2] Goldschmidt and Euler, *Ber.*, 55, 616 (1922).

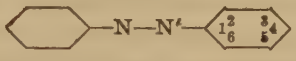
[3] N designates the nitrogen atom attached directly to the unsubstituted benzene nucleus, N′, the nitrogen atom in direct union with the nucleus carrying a substituent group.



Having discovered this relationship between structure and behavior on oxidation in those cases where the structures were already determined by phenylhydrazine reduction, we were able to extend it to the determination of the structures of the compounds described in this paper, since each member studied had a *p*-substituent in one nucleus. We have in this way determined the structures of the two isomeric mono-acetyl-*p*-iodohydrazobenzenes, of the single acetyl derivative of *p*-acetoxyhydrazobenzene, which is the N-derivative, of the single mono-acetyl-*p*-carboxyhydrazobenzene, which is also the N-derivative, and of the single mono-acetylbenzenehydrazo-*p*-phenetole, which proved to be the N′-derivative.

The subjoined table summarizes the mono-acetyl hydrazines studied in this and in our previous paper, with the findings as to structure.

TABLE I



Substituent group	Position	CH_3CO- attachment	Method of structure-determination	M. p. (corr.), °C.
CH_3	2	N	Red.	78
CH_3	4	N′	Ox. + red.	140–141
CH_3	4	N	Ox. + red.	124
Cl	4	N′	Ox. + red.	111–112
Cl	4	N	Ox. + red.	123–124
Br	4	N′	Ox. + red.	83
Br	4	N	Ox. + red.	117–118
I	4	N′	Ox.	156–157
I	4	N	Ox.	135–136
COOH	4	N	Ox.	207–208
$OCOCH_3$	4	N	Ox.	105–106
OC_2H_5	4	N′	Ox.	108

The symbol "Ox." signifies dichromate oxidation, and "Red.," phenylhydrazine reduction.

The formation of highly colored products on oxidation of the mono-acetylhydrazo compounds appeared, superficially, to bear a relationship to the behavior of certain hydrazo compounds on treatment with mineral acids. Jacobson and Kunz[4] reported the significant fact that *p*-acetamidohydrazobenzene in acid solution became deep blue in color. We have noticed that other hydrazo compounds behave in this manner. Hydrazobenzene, hydrazo-*p*-phenetole, *p*-methyl-, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzene suspended in 10% hydrochloric acid at room temperature, and then exposed to the air for several days, yield blue or violet solutions.

[4] Jacobson and Kunz, *Ann.*, **303**, 363 (1898).

The formation of these colored products is undoubtedly caused by air oxidation of the original unrearranged products, since hydrazobenzene, even after the development of color when treated in this manner, contains no detectable amount of benzidine. A solution containing the rearranged products of hydrazobenzene developed no color when similarly treated. The colors can be developed in much shorter time by the addition of hydrogen peroxide.

The oxidation of the hydrazo compounds in the presence of hydrochloric acid, furthermore, was found to be quite parallel with the oxidation of their acetyl derivatives by potassium dichromate; the hydrazo compounds which yielded N-acetyl derivatives were found to give brown solutions on air oxidation, presumably representing the formation of the corresponding azo compounds, while those which gave the N′-acetyl derivatives were readily oxidized to deep red or violet colored products. This behavior is most readily explained by assuming that the hydrazo compounds in acid solution form mono salts, which may involve the N- or N′-atom, and oxidize to new colored substances on the one hand, or to the azo compounds, on the other, depending upon the nitrogen atom involved in salt formation, in a manner analogous to the behavior of their acetyl derivatives. The formation of mono salts in the hydrazo series is in harmony with the fact that hydrazine and many of its simple derivatives function chiefly as monoacid bases. Acylation and salt formation of amines, furthermore, appear in the present work to be quite parallel, as in the previously reported cases of phenylhydrazine[5] and methylhydrazine.[6]

It may therefore be said with some assurance that some of the unsymmetrical hydrazo compounds studied by us yield only one mono salt when treated with strong acids, while others yield two isomeric mono salts in approximately equal amounts.

Consideration of the products of rearrangement of the seventy-eight hydrazo compounds described by Jacobson[7] reveals the interesting fact that they show a marked tendency to yield exclusively semidines on the one hand, or diphenyloids on the other. There appear to be only eight outstanding exceptions to this rule, comprising a group in which each member yields both diphenyloids and semidines simultaneously, and in nearly equal amounts; among the eight exceptions occur the members each of which this research has shown to yield two isomeric acetyl derivatives in nearly equal amounts. Thus, benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzenes each yield both diphenyloids and semidines. These facts suggest that the salts of hydrazo compounds are involved in their rearrangement, and, further, that the formation of a

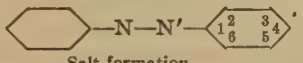
[5] E. Fischer, *Ann.*, **190**, 131 (1878).
[6] Von Brüning, *ibid.*, **253**, 10, 12 (1889).
[7] Jacobson, *ibid.*, **428**, 90–97 (1922).

salt of definite structure precedes the formation of a definite type of rearrangement product. Examination of Jacobson's[7] summary of the rearrangement of the various symmetrical hydrazo compounds (the structures of whose mono salts are known), supplemented by our own observations as to the structures of the salts of various unsymmetrical hydrazo compounds, discloses the following interesting relationship: when salt formation takes place on a nitrogen atom attached to an aryl nucleus in which the *p*-position is open, diphenyloids result, while semidines are formed when the salt in question involves a nitrogen atom attached to a nucleus carrying a *p*-substituent.

Considering the problem from this point of view, it seems that the type of rearranged product is determined by the structure of its mono salt. The tendency to rearrange to one type is so strong that it will often occur even with displacement of para groups already in the ring. However, the character and position of groups (other than para) undoubtedly have an influence, and determine the details within the two main types. It is in the latter sense that Jacobson's[7] rules apply.

It is planned to study other members of the group to determine whether their behavior on acetylation and on oxidation in acid solution is in harmony with the above generalizations. Table II illustrates the relationship between salt structure and type of rearrangement undergone by those hydrazo compounds the structure of whose mono salts is established by this investigation.

TABLE II



Substituent group	Position	Salt formation on	Type of rearrangement
COOH	(4)	N	Diphenyloid
$OCOCH_3$	(4)	N	Diphenyloid
CH_3	(2)	N	Diphenyloid
OC_2H_5	(4)	N′	Semidine
Cl	(4)	N + N′	Diphenyloid + semidine
Br	(4)	N + N′	Diphenyloid + semidine
I	(4)	N + N′	Diphenyloid + semidine
CH_3	(4)	N + N′	Diphenyloid + semidine

By extending this relationship to benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo and *p*-iodohydrazobenzenes, it may be concluded that diphenyloid rearrangement is preceded by formation of the N-salts, and semidine rearrangement by the formation of N′-salts.

A criticism of the hypothesis of Frantzen and Furst,[8] may also be offered. These authors suggest that the benzidine and semidine rearrangements involve the formation of mono salts which then separate into the corresponding amine and halamine

[8] Frantzen and Furst, *Ann.*, **412**, 19 (1917).

$$ArNH_2Cl—NHAr' \longrightarrow ArNHCl + Ar'NH_2$$

The latter are supposed to react, either as such or with intermediate rearrangement of the halamine to the *o*- or *p*-quinol form, to yield the final rearrangement products. Jacobson[9] has pointed out that this scheme does not harmonize with the "maintenance of the aryl combination" in the rearranged products, *i. e.*, the fact that the products of rearrangement always contain the original combination of aryl groups. He says that salt formation and breakdown in only one sense must be assumed in order that the aryl combination remain fixed. Our work has shown that this assumption cannot be made in those cases where the formation of two acetyl derivatives shows the ability of the compound in question to form two different salts. In those cases where only one acetyl derivative is formed, and hence only one salt, the hypothesis is on surer ground. Here only one type of amine and halamine is possible and the aryl combination is maintained.

Experimental Part

The preparation of the azo compounds, their reduction and the formation and separation of their acetyl derivatives were carried out as outlined in an earlier communication.[1] The experimental details of these operations will therefore be omitted in the present report.

Azo Compounds.—*p*-Iodoazobenzene, m. p. 105°, in agreement with Noelting and Werner;[10] *p*-carboxyazobenzene, made by condensation of *p*-aminoethylbenzoate with nitrosobenzene followed by saponification of the ester with alcoholic potassium hydroxide, m. p. 237–238° (corr.), in agreement with Jacobson and Steinbrenk;[11] *p*-acetoxyazobenzene, m. p. 82–83°. Wallach and Kiepenheuer[12] reported 84–85°; benzeneazo-*p*-phenetole, m. p. 77–78°, in agreement with Jacobson and W. Fischer.[13]

Hydrazo Compounds.—*p*-Iodohydrazobenzene, m. p. 105–106°, in agreement with Noelting and Werner;[10] *p*-carboxyhydrazobenzene, m. p. 192–193° (corr.), in agreement with Jacobson and Steinbrenk;[11] *p*-acetoxyhydrazobenzene, pearly plates from 95% alcohol, m. p. 117–118° (corr.).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: N, 11.57. Found: (micro Dumas) N, 11.14.

Acetylhydrazo Compounds.—The more important characteristics of the new acetyl compounds are listed below. N-Acetyl-*p*-iodohydrazobenzene, clusters of needles from 95% alcohol, m. p. 135–136° (corr.).

Anal. Calcd. for $C_{14}H_{13}N_2OI$: N, 7.95. Found: (micro Dumas) N, 7.45.

N'-Acetyl-*p*-iodohydrazobenzene, prisms from 95% alcohol, m. p. 156–157° (corr.).

Anal. Calcd. for $C_{14}H_{13}N_2OI$: N, 7.95. Found: (micro Dumas) N, 7.89.

N-Acetyl-*p*-carboxyhydrazobenzene, needles from 95% alcohol, m. p. 207–208° (corr.).

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: N, 10.37. Found: (micro Dumas) N, 10.70.

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[9] Jacobson, *Ann.*, **428**, 118 (1922).

[10] Noelting and Werner, *Ber.*, **23**, 3255 (1890).

[11] Jacobson and Steinbrenk, *Ann.*, **303**, 384 (1898).

[12] Wallach and Kiepenheuer, *Ber.*, **14**, 2617 (1881).

[13] Jacobson and W. Fischer, *ibid.*, **25**, 994 (1892).

N'-Acetyl-benzenehydrazo-*p*-phenetole.—This compound was difficult to prepare from the corresponding hydrazo compound because the latter underwent self-oxidation–reduction in the presence of acetic anhydride. The acetyl derivative was obtained in good yield by reduction of benzeneazo-*p*-phenetole with zinc dust and glacial acetic acid in acetic anhydride solution; colorless nodules composed of fine needles, m. p. 108°.

Anal. Calcd. for $C_{16}H_{18}N_2O_2$: N, 1037. Found: (micro Dumas) N, 1054.

N-Acetyl-*p*-acetoxyhydrazobenzene, fine colorless needles from alcohol, m. p. 105–106°.

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: N, 9.86. Found: (micro Dumas) N, 9.22.

Oxidation of the Acetyl Derivatives.—The acetyl derivatives (one mole) were dissolved in glacial acetic acid to form a 10–15% solution, and then shaken for twenty-four hours on a mechanical bottle-shaker with finely ground potassium dichromate (0.66 mole). The N-derivatives yielded deep violet solutions immediately under these conditions, although the completed reaction required ten or more hours. The N-derivatives yielded brown solutions. The solutions were filtered after oxidation to remove any unused potassium dichromate, and then diluted with about five volumes of cold water. After standing overnight, the oxidation products appeared as precipitates which were separated by filtration. The brown solutions yielded in each case the corresponding axo compounds, which were identified by their melting points, and by comparison with authentic samples. The violet solutions yielded dark red crystalline solids. The product so obtained from acetylhydrazobenzene has been recrystallized from petroleum ether and then from alcohol in large plates of dark red color melting at 163° (corr.).

Oxidation of the Hydrazo Compounds.—Small quantities (0.1–0.2 g.) of the hydrazo compounds were suspended in 10% hydrochloric acid at room temperature, and allowed to stand exposed to the air for several days. Those which were found to yield N'-acetyl derivatives were found also to impart a deep violet color to the acid solutions, while those yielding N-acetyl derivatives became brown in color. Benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzenes gave violet solutions in which the brown oxidation products were presumably formed also, although their presence could not be detected visually because of the intense violet color of the solutions. *p*-Acetoxy- and *p*-carboxyhydrazobenzenes, under the same conditions, gave orange-colored solutions. To make certain that the colored products resulted from the oxidation of the hydrazo compounds and not their products of rearrangement, the following experiment was performed: 0.1–0.2 g. of hydrazobenzene was boiled for five minutes with 5 cc. of concentrated hydrochloric acid. A clear solution was obtained, which was diluted with water until the acid concentration was approximately 10%. The solution was exposed to the air for several days, and remained colorless. Further work upon the isolation and identification of these colored air-oxidation products is in progress.

Summary

1. Several new diaryl acyl hydrazines have been prepared.

2. A method for their identification by means of oxidation has been described.

3. The formation of highly colored products from hydrazo compounds in contact with acids has been shown to be caused by air oxidation.

4. A relationship between the salt-forming properties of the nitrogen atoms in hydrazo compounds and their rearrangement in acid solution has been established.

5. The oxidation of hydrazo compounds in acid solution has also been

investigated and correlated with the oxidation of their acetyl derivatives. The phenomena observed have been found to have intimate bearing upon the benzidine and semidine rearrangements.

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